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**(54) Process for Making Conductive Coatings, such as Printed Circuits**

(57) A process for forming a conductive coating on a substrate comprising (1) applying an electrically conductive material to the surface of an uncured or a partially cured organic resin having a tacky surface said resin

being patterned circuitwise on a substrate and, thereafter, in either order, (2) curing said resin to fix the electrically conductive material in position on said surface by either heat or UV radiation, preferably in an inert atmosphere, e.g., nitrogen, and (3) removing any loose electrically conductive material.

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## SPECIFICATION

## Process for Making Conductive Coatings

## 1. Field of the Invention

This invention relates to a process for forming a conductive coating on a substrate.

- 5 The invention also relates to a process for forming conductive coatings on substrates in order to form circuit-boards. 5

## 2. Description of the Prior Art

Conductive coatings are known in the art.

- 10 U.S. 3,412,043 teaches an electrically conductive resinous composition consisting essentially of silver flake, resinous binder and finally divided inert filler in specified weight ratios. Therein one resinous binder is an epoxy resin system which is cured by the addition of an amine curing agent at slightly elevated temperatures. 10

- 15 U.S. 3,746,622 teaches electrically conductive coatings comprising certain epoxy resins, particles of tough polymer having carboxy, hydroxy, amino or isocyanate substituents which cocure with the epoxy resin, finally divided metal particles and a curing agent for the epoxy resin. The curing is obtained by heating the composition at temperatures of 125°C or higher. 15

U.S. 3,968,056 teaches a radiation curable ink comprising a particulated electrically conductive metal containing material in combination with an organic resin binder which is converted to a conductive coating on the surface of a substrate by exposure to either actinic or ionizing radiation.

- 20 Re 30,274 teaches a circuit board for activating high voltage flashlamps, said board including a non-conductive, thermoplastic substrate having a patterned electrically conductive coating on one of its surfaces and defining electrical circuitry for the flashlamps, said coating comprising an organic resin matrix curable by UV radiation and a particulated electrically conductive material selected from the group consisting of a particulated electrically conductive metal and a particulated electrically 20  
25 conductive metal containing material, including mixtures thereof with no more than up to about 15% by weight of said particulated electrically conductive material having an aspect ratio of diameter to thickness of a value greater than 20. 25

- 30 In all of the above prior art compositions used for forming conductive coatings it is to be noted that an electrically conductive material is admixed in with an organic resin which mixture is thereafter exposed to either heat or UV or ionizing radiation. One of the drawbacks of such a system is that, due to the fact that the organic resin is non-conductive but is necessary to act as a matrix for the electrically conductive material and adhere to the substrate in a desired pattern, it is necessary to use large amounts of electrically conductive material, e.g., silver flake or beads, in order to get commercially acceptable conductivity. That is, since the silver flake or beads are dispersed throughout the organic 30  
35 resin and not just in a linear conductive line, it is necessary to use an excessive amount of silver flake or beads which is the expensive portion of the electrically conductive composition. 35

Use of large amounts of electrically conductive material in admixture with the curable resin results in the admixture being so thick and of such high viscosity as to make screen printing of the desired circuitry extremely difficult, if not impossible. On the other hand, when the amount of the electrically conductive material admixed with the curable resin is reduced to allow screen printing, the conductance obtained in the cured admixture is often times not commercially acceptable.

- 40 The present invention provides a process for forming a conductive coating on a substrate which requires less electrically conductive material to obtain the same conductivity. Using the new process a conductive coating can be formed on a substrate using screen printing, or by photoimaging. 40  
45 The present invention provides a process for forming a conductive coating on a substrate comprising 45

(1) applying an electrically conductive material to the surface of an uncured or a partially cured organic resin composition having a tacky surface, said composition being patterned circuitwise on a substrate and, thereafter, in either order,

- 50 (2) curing said composition to fix the electrically conductive material in position on said surface either by UV radiation, preferably, but not necessarily, in an inert atmosphere, or by heat, and 50  
(3) removing any loose electrically conductive material.

- 55 The electrically conductive material herein can be in the form of particles, spheres, beads, powder, fibers, flakes or mixtures thereof. Aside from the noble metals and noble metal coated substrates which can be used as the electrically conductive material herein, the use of other metals such as copper, aluminum, iron, nickel and zinc is also contemplated. Also employable are silver coated glass spheres sometimes referred to as "beads" which have an average diameter of about 6 to 125 microns. These materials are made from glass spheres commonly employed as reflective filler materials and are commercially available. Additionally, glass fibers coated with silver, copper or nickel as shown 55  
60 in French Patent 1,531,272 can also be employed. Electrically conductive material used herein also includes carbon black and graphite. 60

In the instant process the amount of the electrically conductive material needed for conductance is independent of the thickness of the organic resin composition employed. That is, since the

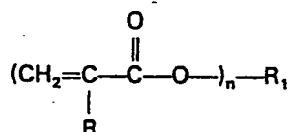
electrically conductive material is applied solely to the top surface of the organic resin, it is immaterial whether the resin has a thickness of 0.5 mils or 20 mils. Operable resin thicknesses herein can range from about 0.05 to 20 mils or more with the preferred range being 0.5 to 2 mils.

The electrically conductive material employed herein can be used in various sizes depending on its form. For best results, the major dimension of the electrically conductive material should be no greater than about 75 microns. However, since the electrically conductive material in the present system is not subjected to screen-printing, which limits its major dimension, even larger particles, flakes or beads having a major dimension of 100 microns or more are operable. Preferably, the electrically conductive material has a major dimension in the range 10 to 60 microns.

The organic resin composition used herein to act as a surface matrix for the electrically conductive material is a solventless, heat and/or UV curable, reactive, liquid organic resin containing at least two olefinic carbon-to-carbon double bonds per molecule. The resin is added in combination with a photoinitiator therefor and in the event of heat curing a thermal initiator. If high energy ionizing radiation is substituted for the UV radiation, no photoinitiator is necessary in the composition.

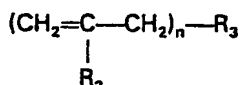
The solventless, curable, reactive liquid organic resins operable herein include, but are not limited to, at least one ethylenically unsaturated member of the group consisting of

(a) a liquid, ethylenically, unsaturated monomer, oligomer or prepolymer of the formula:



wherein R is H or CH<sub>3</sub>, R<sub>1</sub> is an organic moiety and n is 2 to 4,

(b) a polythiol in combination with (a) supra, and  
(c) a polythiol in combination with a liquid ethylenically unsaturated monomer, oligomer or prepolymer of the formula:



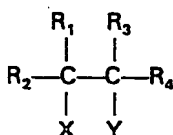
wherein R<sub>2</sub> is H or CH<sub>3</sub>, R<sub>3</sub> is an organic moiety and n is at least 2, and mixtures thereof.

Although the aforesaid organic resins, per se, are operable herein to form useful products, they may also be used in combination with conventional copolymerizable monomeric compounds or reactive diluents. The admixture of the composition of the instant invention with other monomers is employed usually to control viscosity and other application variables such as rate of cure as well as final film or coating properties such as hardness and flexibility. These reactive diluents cocure with the ethylenically unsaturated group member on exposure to UV radiation and heat. Examples of conventional copolymerizable compounds useful as reactive diluents include, but are not limited to, monofunctional acrylic esters, monofunctional methacrylic esters, styrene, vinyl-toluene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl pyrrolidone, vinyl chloride, vinylidene chloride, butadiene, isoprene, chloroprene, divinyl benzene, di(vinyl-phenyl) carbonate, diallyl phthalate, diallyl carbonate, di-(allylphenyl) carbonate, diallyl fumarate, triallyl isocyanurate, triallyl cyanurate, diallyl chloroendate, diallyl maleate and unsaturated polyesters and mixtures thereof. By the term unsaturated polyesters herein is meant the usual polycondensation products which consist of ester-like linked residues of polyvalent, especially divalent, alcohols, as well as possibly also residues of monovalent alcohols and/or of monovalent carboxylic acids, whereby the residues must contain at least partially unsaturated groups. Examples of acids include maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, succinic acid, glutaric acid, adipic acid, phthalic acid, tetrachlorophthalic acid, hexachloroendomethylenetetrahydrophthalic acid, trimellitic acid, benzoic acid, linseed oil fatty acid and ricinoleic fatty acid and mixtures thereof. Examples of alcohols include ethylene glycol, diethylene glycol, propane, butane and hexane diols, trimethylolpropane, pentaerythritol, butanol and tetrahydrofurfuryl alcohol.

The reactive diluents can be added to the system in amounts ranging up to 90% by weight of the organic resin, preferably 20 to 50% by weight on the same basis.

The thermal initiators used herein are selected from substituted or unsubstituted pinacols.

The substituted or unsubstituted pinacols operable herein as a thermal initiator have the general formula:



wherein  $R_1$  and  $R_3$  are the same or different substituted or unsubstituted aromatic radicals,  $R_2$  and  $R_4$  are substituted or unsubstituted aliphatic or aromatic radicals and X and Y which may be the same or different are hydroxyl, alkoxy or aryloxy.

Preferred pinacols are those wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are aromatic radicals, especially phenyl radical and X and Y are hydroxyl.

Examples of this class of compounds include, but are not limited to, benzopinacol, 4,4'-dichlorobenzopinacol, 4,4'-dibromobenzopinacol, 4,4'-diiodobenzopinacol, 4,4',4'',4'''-tetrachlorobenzopinacol, 2,4-2',4'-tetrachlorobenzopinacol, 4,4'-dimethylbenzopinacol, 3,3'-dimethylbenzopinacol, 2,2'-dimethylbenzopinacol, 3,4-3',4'-tetramethylbenzopinacol, 4,4'-dimethoxybenzopinacol, 4,4',4'',4'''-tetramethoxybenzopinacol, 4,4'-diphenylbenzopinacol, 4,4'-dichloro-4'',4'''-dimethylbenzopinacol, 4,4'-dimethyl-4'',4'''-diphenylbenzopinacol, xanthopinacol, fluorenonepinacol, acetophenonepinacol, 4,4'-dimethylacetophenone-pinacol, 4,4'-dichloroacetophenonepinacol, 1,1,2-triphenyl-propane-1,2-diol, 1,2,3,4-tetraphenylbutane-2,3-diol, 1,2-diphenylcyclobutane-1,2-diol, propiophenone-pinacol, 4,4'-dimethylpropiophenonepinacol, 2,2'-ethyl-3,3'-dimethoxypropiophenone-pinacol, 1,1,1,4,4,4-hexafluoro-2,3-diphenyl-butane-2,3-diol.

As further compounds according to the present invention, there may be mentioned:

benzopinacol-mono methylether, benzopinacol-mono-phenylether, benzopinacol and monoisopropyl ether, benzopinacol monoisobutyl ether, benzopinacol mono (diethoxy methyl) ether and the like.

The pinacol is added to the composition in amounts ranging from 0.01—10%, preferably 0.1—5%, by weight based on the weight of the organic resin.

The thermal initiator can be added to the system in various ways. That is, the thermal initiator, per se, can be admixed with the organic resin. Additionally, it can be admixed with a photoinitiator and added to the organic resin. Furthermore, the thermal initiator can be dissolved or suspended in well known commercially available solvents such as dibutyl phthalate; ketones, e.g., acetone and methylethyl ketone or chlorinated hydrocarbons such as methylene chloride, and then added to the system.

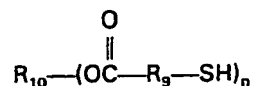
In practicing the instant invention it is sometimes desirable to add a polythiol to the composition prior to curing. This is especially true when the ethylenic unsaturation in the organic resin (sometimes hereinafter referred to as a polyene) is an allylic group. In this case, during the curing step, the polythiol adds across the double bond of the allylic group resulting in solid cured materials in a commercially acceptable time period. In the instance where the ethylenic unsaturation in the polyene is an acrylic or methacrylic group, the addition of a polythiol to the system results in a fully cured resin and precludes the occurrence of a tacky surface due to air inhibition of the curing.

As used herein, the term polythiols refers to simple or complex organic compounds having a multiplicity of pendant or terminally positioned —SH functional groups per average molecule.

On the average the polythiols must contain 2 or more —SH groups/molecule and usually have a viscosity range of slightly above 0 to 20 million centipoises (cps) at 70°C, as measured by a Brookfield Viscometer. Included in the term "polythiols" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the viscosity range set out above at 70°C. Operable polythiols in the instant invention usually have molecular weights in the range 94—20,000, preferably 100—10,000.

The polythiols operable in the instant invention can be exemplified by the general formula:  $R_8-(SH)_n$  where n is at least 2 and  $R_8$  is a polyvalent organic moiety free from reactive carbon-to-carbon unsaturation. Thus,  $R_8$  may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P or O but primarily contains carbon-hydrogen, carbon-oxygen or silicon-oxygen containing chain linkages free of any reactive carbon-to-carbon unsaturation.

One class of polythiols operable with polyenes in the instant invention to obtain essentially odorless polythioether products are esters of thiol-containing acids of the general formula  $HS-R_9-COOH$ , where  $R_9$  is an organic moiety containing no "reactive" carbon-to-carbon unsaturation, with polyhydroxy compounds of the general structure  $R_{10}-(OH)_n$ , where  $R_{10}$  is an organic moiety containing no "reactive" carbon-to-carbon unsaturation and n is 2 or greater. These components will react under suitable conditions to give a polythiol having the general structure



wherein  $R_9$  and  $R_{10}$  are organic moieties containing no "reactive" carbon-to-carbon unsaturation and n is 2 or greater.

Certain polythiols such as the aliphatic monomeric polythiols (ethane dithiol, hexamethylene dithiol, decamethylene dithiol, tolylene-2,4-dithiol, etc.) and some polymeric polythiols such as a thiol-terminated ethylcyclohexyl dimercaptan polymer, etc., and similar polythiols which are conveniently and ordinarily synthesized on a commercial basis, although having obnoxious odors, are operable in this invention but many of the end products are not widely accepted from a practical, commercial point of view. Examples of the polythiol compounds preferred for this invention because of their relatively

low odor level include, but are not limited to, esters of thioglycolic acid ( $\text{HS}-\text{CH}_2\text{COOH}$ ), alpha-mercaptopropionic acid ( $\text{HS}-\text{CH}(\text{CH}_3)-\text{COOH}$ ) and beta-mercaptopropionic acid ( $\text{HS}-\text{CH}_2\text{CH}_2\text{COOH}$ ) with polyhydroxy compounds such as glycols, triols, tetraols, pentaols, hexaols, etc. Specific examples of the preferred polythiols include, but are not limited to, ethylene glycol bis (thioglycolate), ethylene glycol bis (beta-mercaptopropionate, trimethylolpropane tris(thioglycolate), trimethylolpropane tris(beta-mercaptopropionate), pentaerythritol tetrakis(thioglycolate) and pentaerythritol tetrakis(beta-mercaptopropionate), all of which are commercially available. A specific example of a preferred polymeric polythiol is polypropylene ether glycol bis(beta-mercaptopropionate) which is prepared from polypropylene ether glycol (e.g., Pluracol P2010, Wyandotte Chemical Corp.) and beta-mercaptopropionic acid by esterification.

Additionally, polythiols operable herein to give cured solid polythioether products with the polyene in the presence of a free radical generator include the mercaptoester derivatives of styrene-allyl alcohol copolymers set out in U.S. Patent No. 3,904,499 and the isocyanurate containing polythiols disclosed in U.S. Patent No. 3,676,440 and liquid thiol-terminated polymers made in accord with U.S. Patent No. 3,258,495, all incorporated hereby by reference. An example of the aforesaid latter type liquid thiol-terminated polymer is CAPCURE 3-800, commercially available from Diamond Shamrock Chemical Company.

The preferred polythiol compounds are characterized by a low level of mercaptan-like odor initially and, after reaction, give essentially odorless polythioether end products which are useful for fixing electrically conductive material in position.

In the case of a polythiol in combination with allylic polyenes the mole ratio of thiol/ene groups for preparing the curable composition is from 0.2/1 to about 2/1 and desirably about 0.75/1 to about 1.5/1 group ratio.

In the case of a polythiol in combination with acrylic components the mole ratio of thiol/ene groups for preparing the curable composition is from 0.01/1 to about 1/1 and desirably about 0.02/1 to about 0.5/1 group ratio.

Prior to curing, the polyene and polythiol components are admixed in a suitable manner so as to form a homogeneous liquid curable mixture. Thus, the polyene and polythiol reactants can be admixed without the necessity of using a solvent at room temperature or slightly elevated temperatures up to about  $40^\circ\text{C}$  when one of the components is a solid or, if desired, the reactants may be dissolved in a suitable solvent and, thereafter, the solvent can be removed by suitable means such as evaporation.

The compositions of the present invention may, if desired, include such additives as antioxidants, inhibitors, fillers, antistatic agents, flame-retardant agents, thickeners, thixotropic agents, surface-active agents, viscosity modifiers, plasticizers, tackifiers and the like within the scope of this invention.

Such additives are usually preblended with the ethylenically unsaturated compound prior to or during the compounding step. Operable fillers which can be added to the system to cut cost include natural and synthetic resins, glass fibers, wood flour, clay, silica, alumina, carbonates, oxides, hydroxides, silicates, glass flakes, borates, phosphates, diatomaceous earth, talc, kaolin, barium sulfate, calcium sulfate, calcium carbonate and the like. The aforesaid additives may be present in quantities up to 500 parts or more per 100 parts of the organic resin by weight and preferably about 0.005 to about 300 parts on the same basis.

Additionally, conventional UV stabilizers and antioxidants such as hydroquinone, tert-butyl hydroquinone, tert-butyl catechol, p-benzoquinone, 2,5-diphenylbenzoquinone, 2,6-di-tert-butyl-p-cresol, etc., are added to the system in conventional amounts ranging from 0.001 to 2.0% by weight of the organic resin.

It preferably is necessary to add photoinitiators in order to initiate the UV reaction. One class of photoinitiators are the aldehyde and ketone carbonyl compounds having at least one aromatic nucleus attached directly to the



group. Various of this type of photoinitiators include, but are not limited to, benzophenone, acetophenone, o-methoxy-benzophenone, acenaphthene-quinone, methyl ethyl ketone, valerophenone, hexanophenone, alpha-phenylbutyrophenone, p-morpholinopropionphenone, dibenzosuberone, 4-morpholino-benzophenone, 4'-morpholinodeoxybenzoin, p-diacetyl-benzene, 4-aminobenzophenone, 4'-methoxyacetophenone, benzaldehyde, alpha-tetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 10-thioxanthene, 3-acetyl-phenanthrene, 3-acetylundone, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthene-9-one, xanthrene-9-one, 7-H-benz[de]anthracene-7-one, 1-naphthaldehyde, 4,4'-bis(dimethylamino) benzophenone, fluorene-9-one, 1'-acetophenone, 2'-acetophenone, 2,3-butanedione, acetophenone, 2,3-butanedione, benz[a]anthracene 7,12 dione, etc. Another class of photoinitiators is the benzoin ethers, such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether and 2,2-dimethoxy-2-phenylacetophenone. A third class of photoinitiators is exemplified by benzil dimethyl

ketal. Other photoinitiators operable herein include triphenylphosphine and tri-*o*-tolyl phosphine. The photoinitiator or mixtures thereof are usually added in an amount ranging from 0.0005 to 30% by weight of the organic resin.

A type of radiation useful herein for curing is ultraviolet light and other forms of actinic radiation which are normally found in radiation emitted from the sun or from artificial sources such as Type RS Sunlamps, carbon arc lamps, xenon arc lamps, mercury vapor lamps, tungsten halide lamps and the like. Ultraviolet radiation may be used most efficiently if the photocurable composition contains a suitable photoinitiator. Curing periods may be adjusted to be very short and hence commercially economical by proper choice of ultraviolet source, photoinitiator and concentration thereof, temperature and molecular weight and reactive group functionality of the organic resin. Curing periods of about 1 second to 10 minutes duration are operable depending on the aforesaid variables.

When UV radiation is used, an intensity of 0.0004 to 60.0 watts/cm<sup>2</sup> in the 200—400 nanometer region is usually employed.

As heretofore stated, the uncured or partially cured organic resin to which the electrically conductive material is added can be formed by screen printing or photoimaging. In the screen printing method, the organic resin admixed with the photoinitiator (and optionally the thermoinitiator if heat is to be used for the final cure) is squeezeed through a screen into a desired circuit pattern. In the instance where the ethylenic unsaturation in the organic resin is an acrylic or methacrylic group, the subsequent direct exposure to UV radiation results in a tacky, uncured surface on the resin due to air inhibition of the curing. The electrically conductive material is sprinkled, dusted or sprayed on this tacky surface and the surface is subjected to a final cure either by UV radiation from the top, bottom (if substrate is UV transparent) or both in an inert atmosphere or by heat, e.g., in a conventional heating oven (air) at a temperature of 50—250°C if a thermal initiator has been added to the system. In the other instances where air does not affect the curing of the organic resin due to the presence of a polythiol admixed therewith, the organic resin is screen printed circuitwise, sprinkled, dusted or sprayed with the electrically conductive material and then subjected to UV radiation in air from the top or from the bottom through a UV transparent substrate or both. Additionally, instead of using UV radiation for final curing, a thermal initiator can be admixed with the original formulation and, after adding the electrically conductive material to the surface of the uncured or partially cured resin, it can be subjected to heat to cure the organic resin and fix the electrically conductive material in position on the surface thereof.

In the case of photoimaging, the non-conductive substrate is coated throughout with a thin coating (up to 5 mils) of the organic resin admixed with the photoinitiator and optionally the thermal initiator. The coating is then exposed to UV radiation through a transparency, the image of which is positive relative to the circuit desired. In the instance where the organic resin employed is one that is not air inhibited, a tacky surface is avoided throughout the exposed area. The transparency is removed and the electrically conductive material is sprayed, dusted or sprinkled on the uncured, unexposed portion of the organic resin, i.e., the circuit desired as patterned by the transparency. The thus coated substrate is then exposed directly to UV radiation in air from the top or from the bottom or both to cure the circuit pattern and fix the electrically conductive material therein. This latter step can also be performed, if a thermal initiator is added to the system, by exposing the coated substrate to heat at a temperature in the range 50—250°C for a time sufficient to cause curing of the organic resin in the circuit pattern thereby fixing in position the electrically conductive material. In using the photoimaging method in the case where the ethylenic unsaturation in the organic resin is an acrylic or methacrylic group, it is necessary to carry out the photoimaging step using UV radiation through a transparency in an inert, e.g., nitrogen atmosphere. In this way the portions exposed to UV radiation will cure clear through and no tacky surface will result. The unexposed portion under the circuit pattern on the transparency will remain uncured. The electrically conductive material is then applied to the uncured circuit pattern on the coated substrate and, thereafter, the pattern is reexposed from top, bottom or both to UV radiation in an inert atmosphere. Additionally, this second curing step can be carried out when a thermal initiator is added to the system by exposing the uncured organic resin with the electrically conductive materials thereon to heat at a temperature 50—250° for a time sufficient to cure the uncured organic resin.

In all of the above procedures loose particles of the electrically conductive material which on application fall or reside on the substrate or the cured coating on the substrate can be removed readily either before the electrically conductive material is fixed in the desired circuit by the final curing or after the final curing step. Such removal before final curing is readily accomplished by conventional means, e.g., brushing off excess electrically conductive material, tapping the substrate on end or by use of an air spray. After final cure, in addition to the methods available before final cure, it is possible to use a water or water detergent spray or bath. The thus removed electrically conductive material can then be reused in the system after reprocessing to remove oxides.

The heating step using a thermal initiator to cure the organic resin and to fix the electrically conductive material in position is usually carried out for a period of 1 to 10 minutes at a temperature of 50—250°C, preferably 80—175°C which is sufficient to fully cure the composition to a solid product. In addition to conventional heat sources such as a heating oven which can be used for the heating step to cure the organic resin, one can also use radiation such as infrared, microwave or radial frequency

which are capable of generating the required temperature within the organic resin for curing.

The following examples will aid to explain, but specifically not limit, the instant invention. Unless otherwise noted, all parts and percentages are by weight.

#### Example 1

##### 5 Preparation of Urethane Triacrylate Oligomer with Diacrylate Diluent

5

To a mixture of 30.035 parts of methylene-bis(cyclohexylisocyanate) containing 0.0275 parts of stannous octoate and 0.506 parts of triphenyl phosphite was added 15.231 parts of hydroxypropyl acrylate. After 2 hours at 50°C, 0.020 parts of hydroquinone monomethyl ether, 0.0275 parts of stannous octoate and 24.5 parts of hexanediol diacrylate were added, followed by 29.562 parts of PLURACOL TP-740 (a triol of MW 730 made by reacting trimethylolpropane with propylene oxide). After 1 hour at 80°C the isocyanate content had reached zero. The resulting urethane triacrylate oligomer and diacrylate diluent will be referred to hereinafter as Prepolymer A.

10

#### Example 2

15 A photocurable, screen-printable organic resin composition was prepared by mixing the following components:

15

Table I

	Components	Parts by Weight	
	Prepolymer A from Example 1	40.4	
	Hexanediol diacrylate	25.9	
20	Trimethylolpropane triacrylate	26.5	20
	Diethoxyacetophenone	1.0	
	Benzophenone	2.0	
	Cab-o-Sil	4.0	
	Phosphorous acid	0.2	

25 The above formulation will be referred to hereinafter as Photo composition A.

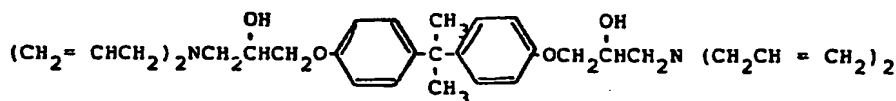
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#### Example 3

To a 5 liter round bottom flask equipped with stirrer, thermometer, Graham (coil) condenser and dropping funnel was charged 1164 g of redistilled, commercially available diallylamine. The flask was flushed with nitrogen and kept under a nitrogen blanket during the reaction. The flask was heated to 80°C with stirring and 1940 g of a Bis-phenol A diglycidyl ether type epoxy resin, commercially available from Shell Chemical Co. under the tradename "EPON 828" was slowly added to the flask by means of the dropping funnel over a 2 hour period while the flask was maintained at a temperature of 80—90°C. After the addition was complete, stirring and heating at 80—90°C were continued for 4 hours. The excess diallylamine (194 g) was vacuum-stripped at 90°C and 1—10 mm Hg. The epoxy tetra-ene product, i.e.,

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35



obtained amounted to 2910 g and will be referred to hereinafter as Prepolymer B.

#### Example 4

40 A photocurable, screen-printable organic resin composition was prepared by mixing the following components:

40

Table II

	Components	Parts by Weight	
	Prepolymer B from Example 3	39.4	
	Triallyl cyanurate	19.5	
45	2,2-dimethoxy-2-phenylacetophenone	2.0	45
	Pentaerythritol tetrakis (beta-mercaptopropionate)	39.4	
	Benzopinacol	1.0	
	FC-430 (coating additive—3M Corp.)	0.24	
	Triphenylphosphine	.20	
50	Stabilizers		50
	pyrogallol	.10	
	phosphorous acid	.02	

The above formulation will be referred to hereinafter as Photo composition B.

#### Example 5

To 10 parts of Photo composition A from Example 2 were added 0.1 part of benzopinacol. This admixture will be referred to hereinafter as Photo composition C.

#### 5 Example 6

Photo composition A from Example 2 was screenprinted in a line circuit pattern (0.64 cm×10.16 cm) onto a Mylar substrate through a 140 mesh Nylon screen. The coated substrate was exposed to UV radiation from an Addalux medium pressure Hg lamp (56 mW/cm<sup>2</sup>) for 2 minutes in air. The thus exposed composition adhered to the Mylar substrate but had a tacky, partially cured top surface. Silver in the form of silver flake (—325 mesh) was sprinkled on the tacky surface of the composition. Excess silver was removed from the substrate by brushing and the silver coated tacky composition was reexposed to the Addalux lamp for 2 minutes in a nitrogen atmosphere. A totally cured solid composition of 4.2±.2 mils thickness with the silver fixed in an embedded position on its surface was obtained. The resultant conductive silver coating weighed 0.099 g and had a specific resistivity of 1.43×10<sup>-2</sup> ohm-cm.

This example was repeated. The resultant conductive silver coating weighed 0.103 g and had a specific resistivity of 1.88×10<sup>-2</sup> ohm-cm.

#### Example 7

Photo composition A from Example 2 was screen-printed in a line circuit pattern (0.64 cm×10.16 cm) onto a Mylar substrate through a 140 mesh Nylon screen. The coated substrate was exposed to UV radiation from an Addalux medium pressure Hg lamp (56 mW/cm<sup>2</sup>) for 2 minutes in air. The thus exposed composition adhered to the Mylar substrate but had a tacky, partially cured top surface. Silver in the form of silver coated glass beads (8 wt% silver) was sprinkled on the tacky surface of the composition. Excess silver beads were removed from the substrate by brushing and the silver bead coated tacky composition was reexposed to the Addalux lamp for 2 minutes in a nitrogen atmosphere. A totally cured solid composition (4.9±.2 mils thick) with the silver fixed in an embedded position on its surface was obtained. The resultant silver coated beads weighed 0.078 g and the conductive coating had a specific resistivity of 5.6×10<sup>-1</sup> ohm-cm.

#### Example 8

Photo composition C from Example 5 was screenprinted in a circuit pattern (0.64 cm×10.16 cm) onto a Mylar substrate through a 140 mesh Nylon screen. The coated substrate was exposed to UV radiation from an Addalux medium pressure Hg lamp (56 mW/cm<sup>2</sup>) for 2 minutes in air. The thus exposed composition adhered to the Mylar substrate but had a tacky, partially cured top surface. Silver in the form of silver coated glass beads (8 wt. % silver) was sprinkled on the tacky surface of the composition. Excess silver was removed from the substrate by brushing and the silver coated tacky composition was heated at 160°C in an air oven for 5 minutes. A totally cured solid composition (4.8±.2 mils thick) with the silver fixed in an embedded position on its surface was obtained. The resultant silver coated beads weighed 0.0508 g and the conductive coating had a specific resistivity of 2.3×10<sup>-3</sup> ohm-cm.

This example was repeated. The silver coated glass beads in the line circuit weighed 0.035 g and the conductive coating had a specific resistivity of 1.48×10<sup>-3</sup> ohm-cm.

#### Example 9.

Photo composition B from Example 4 was coated all over one surface of a Mylar substrate to a thickness of 1 mil. The coating was then exposed to UV radiation from an Addalux medium pressure Hg lamp (56 mW/cm<sup>2</sup>) through a transparency, the image of which is positive relative to a line circuit of 9.0 cm×0.4 cm. The exposure was for 2 minutes resulting in a solid cured composition in all the exposed areas. Silver in the form of silver coated glass beads (8 wt. % silver) was sprinkled on the uncured unexposed liquid portion of the composition, and the excess was brushed off the cured coating on the substrate. The substrate was placed in an air oven and heated at 150°C for 10 minutes. A totally cured solid composition with silver beads fixed in an embedded position in the circuit pattern resulted. The resultant silver coated beads weighed 0.062 g and the conductive coating had a specific resistivity of 2.03×10<sup>-2</sup> ohm-cm.

It should be understood that in order to obtain the maximum strength, solvent resistance, creep resistance, heat resistance and freedom from tackiness, the reaction components consisting of the polyenes and polythiols of this invention are formulated in such a manner as to give solid, crosslinked, three dimensional network polythioether polymer systems on curing. In order to achieve such infinite network formation, the individual polyenes and polythiols must have a functionality of at least 2 and the sum of the functionalities of the polyene and polythiol components must always be greater than 4. Blends and mixtures of the polyenes and the polythiols containing said functionality are also operable herein.



### Claims

1. A process for forming an electrically conductive circuit pattern on a substrate comprising
    - (1) applying an electrically conductive material to the surface of an uncured or a partially cured organic resin composition having a tacky surface, said composition being patterned circuitwise on a substrate and, thereafter, in either order,
    - (2) curing said composition to secure the electrically conductive material in position on said surface by either heat or UV radiation, and
    - (3) removing any loose electrically conductive material.
  2. A process according to claim 1 which comprises
    - (1) printing on the substrate a desired circuit pattern of a UV curable composition comprising
      - (a) an ethylenically unsaturated compound of the formula:
 
$$\begin{array}{c} (\text{CH}_2=\text{C}-\text{C}-\text{O})_n-\text{R}_1 \\ | \quad || \\ \text{R} \quad \text{O} \end{array}$$

wherein R is H or CH<sub>3</sub> and R<sub>1</sub> is an organic moiety with the valence of n and n is 2 to 4, and

    - (b) a photoinitiator;
  - (2) exposing the said composition to UV radiation for a time sufficient to obtain an adherent, solid, printed circuit pattern with a tacky surface;
  - (3) coating at least the tacky surface of the said composition with the electrically conductive material, and then, in either order;
  - (4) reexposing at least the coated tacky surface of the said composition to UV radiation in a substantially oxygen-free atmosphere to solidify said tacky surface and form an electrically conductive circuit thereon; and
  - (5) removing any loose electrically conductive material.
3. A process according to claim 1 which comprises
  - (1) printing on the substrate a desired circuit pattern of a UV and heat curable composition comprising
    - (a) an ethylenically unsaturated compound of the formula:
 
$$\begin{array}{c} (\text{CH}_2=\text{C}-\text{C}-\text{O})_n-\text{R}_1 \\ | \quad || \\ \text{R} \quad \text{O} \end{array}$$

wherein R is H or CH<sub>3</sub> and R<sub>1</sub> is an organic moiety with the valence of n and n is 2 to 4,

    - (b) a photoinitiator, and
    - (c) a thermal initiator;
  - (2) exposing the said composition to UV radiation for a time sufficient to obtain an adherent, solid, printed circuit pattern with a tacky surface;
  - (3) coating at least the tacky surface of said composition with an electrically conductive material, and then, in either order;
  - (4) exposing the coated composition to a temperature in the range 50—250°C to solidify said tacky surface and form an electrically conductive circuit thereon; and
  - (5) removing any loose electrically conductive material.
4. A process according to claim 3 wherein the thermal initiator is a substituted or unsubstituted pinacol.
5. A process according to claim 1 which comprises
  - (1) coating the substrate with a UV curable composition comprising
    - (a) a solventless, curable, reactive, liquid organic resin containing at least 2 olefinic carbon-to-carbon double bonds per molecule and
    - (b) a photoinitiator;
  - (2) exposing said coating to UV radiation through an imaged transparency, the image of which is positive relative to the desired circuit to form a cured adherent coating on the substrate in the exposed, non-circuit area;
  - (3) coating the unexposed, uncured circuit area of the composition with an electrically conductive material and then, in either order;
  - (4) reexposing at least the uncured area to UV radiation to cure said area and secure the electrically conductive material on the surface thereof; and
  - (5) removing any loose electrically conductive material.
6. A process according to claim 1 which comprises
  - (1) coating the substrate with a UV and heat curable composition comprising
    - (a) a solventless, curable, reactive, liquid organic resin containing at least 2 olefinic carbon-to-carbon double bonds per molecule,
    - (b) a photoinitiator, and
    - (c) a thermal initiator;

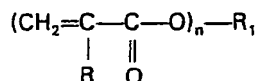
(2) exposing the said coating to UV radiation through an imaged transparency, the image of which is positive relative to the desired circuit to form a cured, adherent coating on the substrate in the exposed, non-circuit area;

(3) coating the unexposed, uncured circuit area of the composition with an electrically conductive material and then, in either order;

(4) exposing at least the uncured circuit area to a temperature in the range 50—250°C to cure said area and secure the electrically conductive material on the surface thereof; and

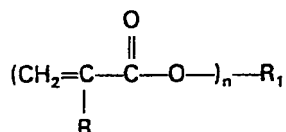
(5) removing any loose electrically conductive material.

7. A process according to claim 5 or 6 wherein the organic resin consists essentially of an ethylenically unsaturated compound of the formula:



wherein R is H or CH<sub>3</sub> and R<sub>1</sub> is an organic moiety with the valence of n and n is 2 to 4, and the exposure to UV radiation is carried out in a substantially oxygen-free atmosphere.

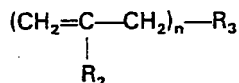
8. A process according to claim 1 wherein the organic resin in the organic resin composition is (a) a liquid, ethylenically, unsaturated monomer, oligomer or prepolymer of the formula:



wherein R is H or CH<sub>3</sub>, R<sub>1</sub> is an organic moiety and n is 2 to 4,

(b) a polythiol in combination with (a) or

(c) a polythiol in combination with a liquid ethylenically unsaturated monomer; oligomer or prepolymer of the formula:



wherein R<sub>2</sub> is H or CH<sub>3</sub>, R<sub>3</sub> is an organic moiety and n is at least 2, and mixtures thereof.

9. A process according to any of claims 1 to 8 wherein the said composition is cured by UV radiation in an inert atmosphere.

10. A process according to any of claims 1 to 9 wherein the composition contains a reactive diluent.

11. A process according to any of claims 1 to 10 wherein the electrically conductive material is in particle, sphere, powder, fibre, flake form or a mixture thereof.

12. A process according to claim 1 substantially as described in any one of Examples 6 to 9.

13. Electrically conductive circuit patterns when produced by the process of any of claims 1 to 12.

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